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(19) (CA) **CANADIAN PATENT** (12)

(54) Continuous Procedure for Obtaining Pure Terephthalic
Acid and Glycol Starting from Polyethylene
Terephthalate Waste

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Continuous method for obtaining pure terephthalic acid and glycol on the basis of polyethylene terephthalic waste, characterized by the fact that it comprises the following stages: subject to hydrolysis, in the presence of a certain amount of decolorizing carbon, a quantity of polyethylene terephthalate waste with water, at a high pressure and at a temperature which varies between 200°C and 300°C; filter the hydrolyzate also under conditions of high temperature and pressure; crystallize the terephthalic acid of the filtered solution by means of cooling in the crystallization receptor at a final temperature which varies between -10°C and 200°C; filter or centrifuge to separate the filtrate crystals; wash and dry the pure terephthalic acid crystals; and, on the other hand, distill the filtrate so as to obtain pure glycol.
2. Continuous method for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste in accordance with what is claimed in claim 1, characterized furthermore by the fact that the quantity of water used is equal or greater than that required to keep the terephthalic acid dissolved under hydrolysis conditions.
3. Continuous method for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste in accordance with what is claimed in claim 1 and 2, characterized also by the fact that the time of the hydrolysis reaction is between 5 minutes and 6 hours.
4. Continuous method for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste in

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accordance with what is claimed in claims 1 to 3, also characterized by the fact that the quantity of the decolorizing carbon added is between 0.1% and 30%, with respect to the quantity of waste treated.

5. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in claims 1-3, characterized also by the fact that the cooling is carried out by venting the pressure in the crystallizer.

6. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate, in accordance with what is claimed in claims 1-3, characterized also by the fact that the final crystallization pressure is equal to atmospheric pressure.

7. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in claims 1-3, characterized also by the fact that the final crystallization pressure is lower than atmospheric pressure but greater than 1 mm Hg absolute, using a vacuum device.

8. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in claims 1-3, also characterized by the fact that the final crystallization pressure is greater than the atmospheric pressure but less than 15 atmospheres.

9. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in claims 1-3, characterized

also by the fact that the cooling is carried out by means of a cold surface, such as a jacket in the crystallizer, or by means of a coil in the crystallizer, or using both a jacket and a coil.

10. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in claims 1-3, also characterized by the fact that the cooling is carried out by means of any combination of a cold surface and a simultaneous venting of the pressure.

11. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in claims 1-3, also characterized by the fact that the crystallization time is between 5 minutes and 5 hours.

12. Continuous method according to claim 1 wherein said hydrolysis temperature is attained by introducing steam under pressure directly to said hydrolysis stage.

13. Continuous method according to claim 1 or 12 wherein said polyethylene terephthalate waste and water are agitated during said hydrolysis stage in a reaction zone.

14. Continuous method according to claim 1 or 12 wherein in high-pressure, saturated steam is injected continuously from a lower part of a hydrolyzer to said hydrolysis stage.

15. Continuous method according to claim 1 or 12 wherein discharge of said hydrolyzate is adjusted such that it is agitated by excess steam at the hydrolysis stage.

16. The continuous process for obtaining pure terephthalic acid and glycol from polyethylene terephthalate waste

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comprising the steps:

subjecting polyethylene terephthalate waste to neutral, aqueous hydrolysis in a hydrolysis zone at a temperature of between 200°C and 300°C and superatmospheric pressure of at least 15 atmospheres, said hydrolysis being conducted in the presence of decolorizing carbon in an amount of between 0.1 to 30 weight percent of said waste;

removing supernatant liquid from said hydrolysis zone and filtering said liquid under conditions of high temperature and pressure to recover an aqueous solution of terephthalic acid and glycol;

passing said aqueous solution of terephthalic acid and glycol to a crystallization zone and cooling said solution to a temperature of between -10°C and 200°C in said crystallization zone to thereby cause crystallization of terephthalic acid from said solution;

separating by filtering or centrifuge said terephthalic acid crystals from the liquid in said crystallization zone and washing and drying said crystals to provide pure terephthalic acid;

passing the liquid from said crystallization zone to a distillation zone and distilling said liquid to provide pure glycol.

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CONTINUOUS PROCEDURE FOR OBTAINING PURE TEREPHTHALIC ACID AND GLYCOL
STARTING FROM POLYETHYLENE TEREPHTHALATE WASTE

Abstract of the invention

A procedure is described to obtain pure terephthalic acid and glycol, which consists in carrying out, in a continuous manner and in the presence of decolorizing carbon, an aqueous and neutral hydrolysis of polyethylene terephthalate waste, under high temperature and pressure conditions, continuously filtering the product at the hydrolysis temperature and crystallizing the terephthalic acid, while the mother liquors are subjected to distillation in order to obtain the glycol.

Basis of the invention

Field of the invention

The invention under consideration is related to a continuous method which permits obtaining pure terephthalic acid and glycol and more specifically, it is related with a procedure which utilizes as a raw material polyethylene terephthalate waste and in which it is not necessary to first separate the crude or impure terephthalic acid in order to purify it in a subsequent stage by means of one

of the known procedures. In the method of the invention under consideration, the product is obtained pure and can be utilized as a raw material once again in the preparation of the polyethylene terephthalate utilized in the manufacture of polyester fibers and plastics.

Description of the prior art

Neutral hydrolysis of polyethylene terephthalate at a high temperature and pressure is a known operation (see Ludewig, H. and Ramm, H.: German Economic Patent 14,854 (1956) and
 10 Littmann, E. On the preparation of terephthalic acid or its dimethyl or diglycol ester from polyethylene terephthalate. Abh. d. Deutsch. Akad. d. Wiss. Kl. F. Chem, Geolog. und Biochemie I (1963) 401-411).

Neither of the methods described in the aforementioned references mentions the addition of decolorizing carbon in the hydrolysis stage.

On the other hand, the methods mentioned there are discontinuous methods in which, moreover, the terephthalic acid is obtained impure so that once it is separated, it will have
 20 to be subjected to some purifying procedure.

In this way, the methods to which reference has been made require a subsequent purifying stage which may be the dissolution of the product in sodium hydroxide and subsequently, a reprecipitation by means of acidification, either with treatment of the solution obtained or without an intermediate treatment, or by having recourse to transformation to the dimethyl ester, which is subsequently sublimed.

Summary of the invention

The method of the invention under consideration has
 30 as its object the obtaining of terephthalic acid and glycol in which the purification is undertaken simultaneously with

the hydrolysis.

Another object of the invention under consideration is to provide a method for the preparation of pure terephthalic acid and glycol in which the number of stages of the process is reduced.

An advantage of the method of the invention under consideration is that upon reducing the number of stages of the process - that is, upon eliminating the subsequent stage of purifying the terephthalic acid - the cost of the product is lowered.

Another advantage of the invention under consideration is that it permits the utilization of the polyethylene terephthalate in a simple manner.

Yet another advantage of the method of this invention is that due to the simplicity of the equipment utilized, it can be carried out with relative ease.

According to the present invention, there is now provided a continuous method for obtaining pure terephthalic acid and glycol on the basis of polyethylene terephthalic waste, characterized by the fact that it comprises the following stages: subject to hydrolysis, in the presence of a certain amount of decolorizing carbon, a quantity of polyethylene terephthalate waste with water, at a high pressure and at a temperature which varies between 200°C and 300°C; filter the hydrolyzate also under conditions of high temperature and pressure; crystallize the terephthalic acid of the filtered solution by means of cooling in the crystallization receptor at a final temperature which varies between -10°C and 200°C; filter or centrifuge to separate the filtrate crystals; wash and dry the pure terephthalic acid crystals; and, on the other hand, distill the filtrate so as to obtain pure glycol.

Preferably, the quantity of water used is equal or greater than that required to keep the terephthalic acid dissolved under hydrolysis conditions.

The present invention may also be defined as the continuous process for obtaining pure terephthalic acid and glycol from polyethylene terephthalate waste comprising the steps: subjecting polyethylene terephthalate waste to neutral, aqueous hydrolysis in a hydrolysis zone at a temperature of between 200°C and 300°C and superatmospheric pressure of at least 15 atmospheres, said hydrolysis being conducted in the presence of decolorizing carbon in an amount of between 0.1 to 30 weight percent of said waste; removing supernatant liquid from said hydrolysis zone and filtering said liquid under conditions of high temperature and pressure to recover an aqueous solution of terephthalic acid and glycol passing said aqueous solution of terephthalic acid and glycol to a crystallization zone and cooling said solution to a temperature of between -10°C and 200°C in said crystallization zone to thereby cause crystallization of terephthalic acid from said solution; separating by filtering or centrifuge said terephthalic acid crystals from the liquid in said crystallization zone and washing and drying said crystals to provide pure terephthalic acid; passing the liquid from said crystallization zone to a distillation zone and distilling said liquid to provide pure glycol.

Detailed description of the invention

According to the preferred method of this invention, the polyethylene terephthalate waste is supplied in the form of granules or yarns or in any other form suitable for handling, to the melting chamber of a screw-type extruder so that the extruder, in turn, feeds it, in a continuous manner, to a hydrolyzer. Alternately, the polymer can also be melted and

injected continuously into the hydrolyzer in this state by means of a high-pressure pump.

In a simultaneous manner, water is injected into said hydrolyzer in a suitable proportion - that is, between 3 to 20 times the amount of the polymer. The water can be introduced cold or hot. In turn, the decolorizing carbon is added in a proportion between 0.1% and 30% (with respect to the quantity of the treated waste), feeding it to the hydrolyzer either with the polymer or suspended in water. Also, a large amount can be
10 introduced in bulk intermittently into the hydrolyzer every so often. The hydrolyzer utilized can be of any type - that is, it can be cylindrical vertical, horizontal or inclined, or it can be the U-shaped type, either vertical, horizontal or inclined.

The hydrolyzer, in turn, should be equipped with a source of heating which can be a jacket into which a heating fluid is introduced; this fluid can be diphenyl-diphenyl oxide or a hot oil or steam. The heating source can also be an interior or exterior coil, using one of the fluids previously
20 mentioned.

Heating can also be provided by means of live steam at high pressure, which is introduced directly into the hydrolyzer.

Preferably, the hydrolyzer should be equipped with devices which impart a slight agitation.

When the equipment is put into operation, the polymer which has not yet been hydrolyzed will be found in the lower part. This is also true for the greater part of the carbon, whereas, on the other hand, the supernatant liquid will be an
30 aqueous solution of terephthalic acid and glycol with some proportion of the decolorizing carbon utilized, which will be suspended in the solution.

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This solution is subjected to a filtering operation under the temperature and pressure conditions in which the hydrolysis is carried out, with the object of eliminating the carbon and all the impurities adsorbed by it. This filtration can be carried out in many diverse ways but the use of a heated cartridge filter is particularly preferred; this is located next to the hydrolyzer - that is, said filtration can be undertaken by means of cartridges which are installed directly within the hydrolyzer.

10 Once the solution is filtered, the pressure to which it is subjected is released and it is sent to a continuous crystallizer which may be at atmospheric pressure, at a pressure higher than atmospheric pressure, or at a pressure lower than atmospheric pressure.

This crystallizer can be equipped with a cooling jacket or a coil, or cooling may be attained by simply venting the pressure.

residual polar solvent (e.g. methanol) used for the desorption operation is driven out of the column by heating and preferably a volatile aliphatic hydrocarbon, e.g. hexane either in the vapour phase or as a superheated liquid. The formation of azeotropic mixtures is also helpful in this case. Herein the first step is called "desorption" and the second step "reactivation".

Pretreatment, adsorption and desorption are preferably carried out at temperatures from 15 to 75°C, more preferably not in excess of 60°C, but pretreatment in particular may be carried out at temperatures from 30 to 110°C and adsorption and desorption at 40 to 80°C. Adsorption is preferably effected in particular at 30 to 60°C, particularly approximately between 20 and 50%.

Reactivation is preferably carried out between 50 to 170°C. Substantially less bleaching aid or active carbon is used in the pre-treatment step than adsorption agent, from 0.5 to 5% by weight of the fat being adequate for the former, but with preferably a fat:adsorbent ratio from 10:1 to 1:1 by weight of the fat. Preferably both the pre-treatment and adsorption steps are applied to the same solution of fat.

A Suitable bleaching earths for use in the invention include activated Fuller's earth, for example Tonsil* and Fulmont, Lucilite, Kieselsäure of Degussa. Granulated or non-granulated active carbon, e.g. Norit*, may alternatively or in addition be used. Bleaching earths are usually acid-activated natural earths of structures typified by Montmorillonit and Bentonit. Acid treatment increases their propensity for adsorption of highly polar organic compounds including highly polar pigments, e.g. chlorophyll. These earths are not suitable for the adsorption of bulk amounts of diglycerides etc, but very

*Trade marks

Note 3. The greater the temperature, the higher will be the rate of the reaction, with the pressure in the equipment being greater at the same time.

Note 4. The pressure is a function of the temperature.

Note 5. The residence time required will depend on the temperature used and on the morphology of the polymer.

Note 6. The residence time in the crystallizer will depend on the average size of the crystal desired, with the crystal being larger, the greater the residence time.

In accordance with the data previously indicated, the method of the invention can be carried out under conditions which are different up to a certain point, and it can be modified in accordance with the level of production required.

Also, very different heating sources can be used, with the needed changes also made in accordance with the morphology and the quality of the waste which is utilized as a raw material.

There will also be variations in accordance with the characteristics of purity and size of the crystal desired in the terephthalic acid produced.

Furthermore, the economic aspect will also influence the selection of the equipment to be employed.

Taking into consideration all the modifications which are comprised within the spirit and scope of the invention, the following will give the preferred embodiment, which is merely for illustrative purposes.

Detailed explanation of the preferred embodiment

In this embodiment, the method of the invention is carried out with the following equipment as illustrated in the drawing:

a) A twin-screw melter extruder which is discharged by means of a multiple-orifice spray head directly into the upper part of the hydrolyzer.

b) A vertical cylindrical hydrolyzer which has a vertical plate in its interior which divides the hydrolyzer into two semicircular sections. Said plate does not have to extend along the whole length but rather will leave a free space both in the upper as well as the lower parts. The supply nozzle which is connected with the extruder is centered over one of the semicircles. On the upper part of the other semicircle there is a bundle of filter cartridges whose outlets are all connected with a common discharge tube. The entry of water is on one side of the hydrolyzer, the side corresponding to the supply of the polymer. The bottom of the hydrolyzer will be equipped with two connections - one which will be used for the introduction of live steam, and the drainage of said hydrolyzer being undertaken through the other connection.

c) A continuous crystallizer which is made up of a vertical tank, a conical bottom and which is equipped with an agitator. The crystallizer is connected to the discharge tube of the filter cartridges on the hydrolyzer by means of a line and an automatic valve which permits the passage of all the liquid in addition to a small quantity of steam which has an agitation function in the hydrolyzer. Said crystallizer also includes an automatic level control discharge device.

d) A continuous centrifuge with a washing device which receives the discharge from the crystallizer and which, in turn, continuously discharges toward the drier.

e) A drier of the vibrating screen type.

f) A distillation column for the recovery of the glycol, on the basis of mother liquors.

What has been described in the preceding is related to the equipment which is particularly preferred for carrying out the method, which consists of the following stages.

The hydrolyzer is loaded with a suitable quantity of water in a continuous manner by means of a metering pump. High-pressure saturated steam is also injected continuously from the lower part

of the hydrolyzer. The waste polymer, together with decolorizing carbon is fed continuously to the hydrolyzer by means of the extruder previously described.

The discharge from the hydrolyzer is adjusted in such a manner that it is slightly agitated by means of the excess steam.

Once the hydrolysis has been undertaken, the product is subjected to filtration in order to be subsequently crystallized. One should indicate that the agitation in the crystallizer has to be the minimum so as to keep the crystals suspended.

The crystals obtained are subjected to a drying stage, which is carried out in a drier which has the flow of air and the temperature suitably adjusted so that neither is excessive.

The distillation of the filtrate, in turn, is carried out in the customary manner in order to obtain the glycol pure.

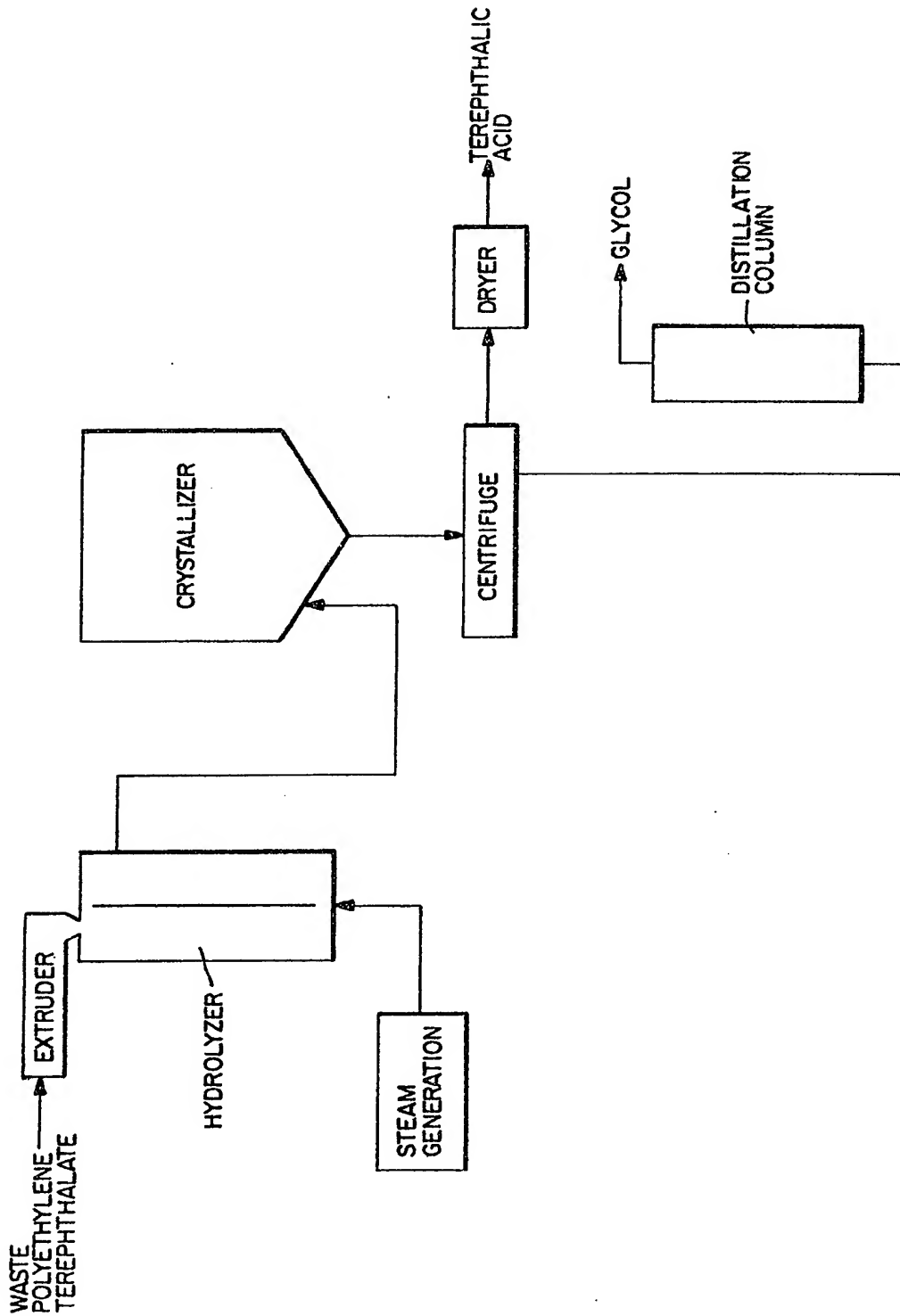
For the case particularly described, the specific reaction conditions are the following:

Water/polymer ratio	12
Carbon/polymer ratio	10%
Hydrolysis temperature	248°C
Hydrolysis pressure	42 atmospheres
Residence time in the hydrolyzer	2 hours
Frequency of carbon discharge every	24 hours
Residence time in the crystallizer	4 hours
Drying temperature	80°C

Although a particularly preferred embodiment has been described and certain changes which can be carried out in the method of the invention under consideration have been outlined, it is obvious that experts in the branch will be able to make, in view of the description under consideration, other modifications, without this deviating from the spirit and scope of the invention so that the preceding description should be considered only for the purposes of illustration and not in any limiting sense.

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